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(71) Applicant: **PRESIDENT AND FELLOWS OF HARVARD COLLEGE** [US/US]; Holyoke Center, Suite 727,
1350 Massachusetts Avenue, Cambridge, MA 02138 (US).

(72) Inventors: **YANG, Hong**; 55 Branch Avenue, Rochester,
NY 14618 (US). **DESCHATELETS, Pascal**; 65 Mt.
Auburn #53, Cambridge, MA 02138 (US). **WHITE-
SIDES, George, M.**; 124 Grasmere Street, Newton, MA
02138 (US).

(74) Agent: **OYER, Timothy, J.**; Wolf, Greenfield & Sacks,
P.C., 600 Atlantic Avenue, Boston, MA 02210 (US).

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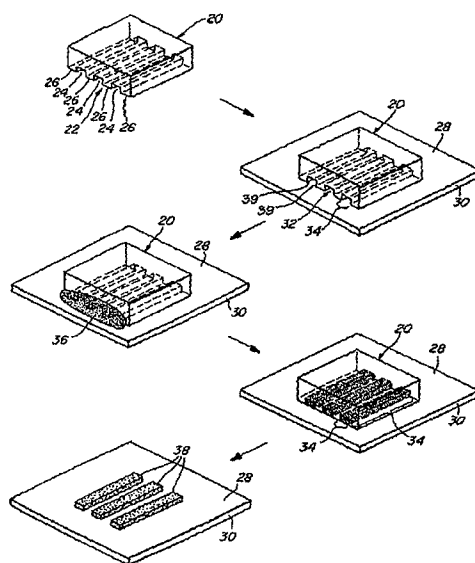
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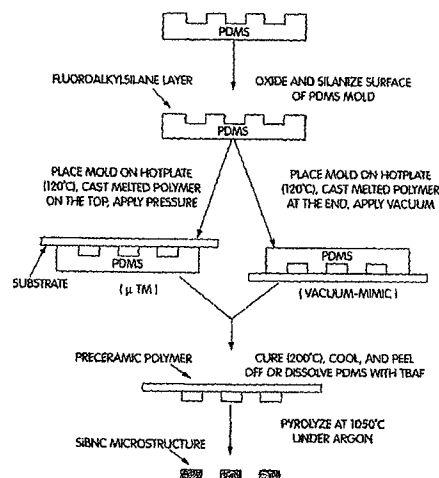
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(54) Title: **FABRICATION OF CERAMIC MICROSTRUCTURES**



A



B

(57) Abstract: The invention provides ceramic molded solid articles and methods for making these articles on the micron scale. Articles are molded from ceramic precursors, optionally using molds including at least one portion that is elastomeric.

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FABRICATION OF CERAMIC MICROSTRUCTURES

Field of the Invention

The present invention relates generally to ceramic solid articles, and more
5 particularly to a method for making these articles on the micron scale by molding them
from ceramic precursors.

Background of the Invention

In the fields of chemistry, biology, materials science, microelectronics, optics,
10 and medicine the development of devices which are small relative to the state of the art
and which are conveniently and relatively inexpensively produced is important.

A well-known method of production of devices, especially in the area of
microelectronics, is photolithography. According to this technique, a negative or
positive resist (photoresist) is coated onto an exposed surface of an article. The resist
15 then is irradiated in a predetermined pattern, and portions of the resist that are irradiated
(positive resist) or nonirradiated (negative resist) are removed from the surface to
produce a predetermined pattern of resist on the surface. This is followed by one or
more procedures. According to one, the resist serves as a mask in an etching process in
which areas of the material not covered by the resist are chemically removed, followed
20 by removal of resist to expose a predetermined pattern of a conducting, insulating, or
semiconducting material. According to another, the patterned surface is exposed to a
plating medium or to metal deposition (for example under vacuum) followed by
removal of resist, resulting in a predetermined plated pattern on the surface of the
material. In addition to photolithography, x-ray and electron-beam lithography can be
25 used in an analogous fashion. Lithography techniques such as those mentioned above
typically require relatively expensive apparatus, and are relatively labor intensive. The
techniques require the design and fabrication of chrome masks, access to clean rooms,
and other requirements commonly known to those skilled in the art.

Microelectromechanical systems are an area of relatively intensive research.
30 These systems involve the fabrication of microscale structures prepared from silicon, or
occasionally from other material such as gallium arsenide, silicon carbide, silicon
nitride, metals, glasses, or plastics, by typical integrated circuit industry
microfabrication techniques such as photolithography or additive/subtractive processes

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such as deposition and etching. While interesting systems have been developed, simplification and increased versatility would be advantageous.

Ceramic structures such as borosilicon carbonitride have numerous applications. Ceramics have found extensive use in connection with products to be used in harsh
5 operating conditions such as when exposed to high temperatures, highly oxidative environments, and when exposed to aggressive chemical conditions. Ceramics are also known for their high strength, hardness, low thermal conductivity, and low electrical conductivity.

U.S. patent no. 5,698,485 (Brück) describes a process for producing ceramic
10 microstructures from mold inserts structured by using the technique lithographie, galvanoförmung, abförmung (LIGA), a lithographic structuring method requiring the use of high energy radiation. LIGA requires a high energy radiation sources such as UV radiation, X-rays, or ion beams. Brück also describes structuring simple geometrically shaped PTFE, PC or PMMA mold inserts through machining.

15 PCT international application number PCT/US98/02573 (Schueller) describes the fabrication of carbon microstructures.

Mat. Res. Innovat. 1999,2,200 (Jungermann, et al.) describes the synthesis of amorphous $\text{Si}_2\text{B}_2\text{N}_5\text{C}_4$. *Nature* 1996, 382, 796 (Riedel, et al.) discloses the synthesis of amorphous silicoboron carbonitride stable up to 2000 °C.

20 These and other techniques for the use of ceramics, including the production of small-scale devices, are useful in some circumstances. However, these techniques typically involve more than a desirable number of fabrication steps, and in many cases it would be advantageous to reduce the cost, and increase versatility, associated with these techniques. Additionally, micromachining is an expensive technique requiring
25 specialty equipment.

Accordingly, it is an object of the invention to provide a technique for forming ceramic solid structures on the micron scale conveniently, inexpensively, and reproducibly.

30 Summary of the Invention

The present invention provides techniques for forming ceramic solid structures. In one aspect, the invention provides a method which involves filling an elastomeric

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mold with a precursor of the ceramic solid structure. The ceramic precursor, in one embodiment, is characterized as a viscous fluid where the viscosity can be attained by setting the precursor and allowing it to maintain its shape. The method can also involve removing the mold from a product of the ceramic precursor. In one embodiment the
5 mold is removed by physically separating the mold from the ceramic precursor. In an alternate embodiment the mold is removed by dissolving the mold. In yet another embodiment, the mold is treated to aid removal of the mold from the ceramic precursor. In a further embodiment, treatment can involve silanizing a surface of the mold. The filling step comprises, according to one embodiment, filling the ceramic precursor
10 between the surface of the mold and a substrate. The mold then is removed from the product of the ceramic precursor and the ceramic precursor remains on the substrate. In a further embodiment, the ceramic precursor is removed from the substrate and a free-standing ceramic solid structure is formed. The free-standing structure is rigid enough to maintain its shape without support along all surfaces of the structure. For example, a
15 small portion of the structure can be held with a support such as a clamp or sharp tweezers.

In another embodiment, the invention provides a method that includes filling the mold with the precursor of the ceramic solid structure, and setting the ceramic precursor. A solid structure, in a shape of the mold, is thereby formed. This method
20 can be carried out using the technique described above, namely, forming the solid structure against the surface of the mold, and can involve other described steps. In one embodiment, the ceramic precursor is set thermally. In another embodiment, the ceramic precursor is set by curing chemically.

In a further embodiment, a method of the invention involves filling,
25 simultaneously, at least two ceramic solid structures from ceramic precursors of the structures. This can involve forming the ceramic precursors against at least two indentations in a surface of a mold, and allowing the ceramic precursors to solidify against the at least two indentations. The precursors then can be heated to form the at least two ceramic solid structures.

30 In the above methods, one or more ceramic precursors can be placed against one or more surfaces of the mold (or one or more indentations in a surface that define two or more molds), setting the ceramic precursor, removing the mold, and thermally

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setting by heating the precursor to form the ceramic solid structure. The method can involve heating the ceramic precursor to form the ceramic solid structure having a dimension of less than 100 μm .

In another embodiment, a method of the invention involves applying the ceramic precursor of the ceramic solid structure to an indentation pattern in the surface of an elastomeric mold, applying the elastomeric mold to a surface of a substrate to encapsulate the ceramic precursor between the substrate surface and the indentation pattern, and curing the ceramic precursor. Then, the mold is removed from the substrate and from the ceramic precursor. The ceramic precursor then is heated to form a free-standing ceramic solid structure having a dimension of less than 100 μm .

According to another aspect, articles are provided in accordance with the invention. In one embodiment, the invention provides a free-standing, ceramic solid structure having a dimension of less than 100 μm . In another embodiment, the dimension is less than 50 μm , and in yet another embodiment less than 25 μm . In other embodiments the structure has a dimension of less than 15 μm , less than 10 μm , less than 5 μm , or less than 1 μm .

The invention provides, according to another embodiment, an article comprising a hexagonal grid.

According to another aspect, a microgear is provided in accordance with the invention.

In yet another aspect, the invention provides a method that involves forming a ceramic solid structure that is a replica of a template structure. The method involves forming the ceramic precursor of the ceramic structure against the surface of a mold cast from the template, and allowing the precursor to take the form characterized by the mold.

Other advantages, novel features, and objects of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings, which are schematic and which are not intended to be drawn to scale. In the figures, each identical or nearly identical component that is illustrated in various figures is represented by a single numeral. For purposes of clarity, not every component is labeled in every figure.

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Brief Description of the Drawings

Fig. 1A illustrates schematically a technique for forming a ceramic solid structure against a surface using a mold, from a ceramic precursor;

Fig. 1B shows another scheme for forming a ceramic solid structure against a surface using a mold, from a ceramic precursor;

Fig. 2 is a schematic illustration of a technique for transferring a ceramic precursor of a ceramic solid structure from indentations in a mold to a substrate surface, forming ceramic solid structures at the surface, and removing free-standing articles from the surface;

Fig. 3 is a photocopy of a scanning electron micrograph (SEM) image of a free-standing ceramic structure;

Fig. 4 is a photocopy of a SEM image of a free-standing, ceramic structure;

Fig. 5 is a photocopy of a SEM image of a free-standing, ceramic structure; and

Fig. 6 is a photocopy of three SEM image of a free-standing, ceramic solid structure, the structure being a micron scale tooth of a gear with an aspect ratio of approximately 3-4 to 1.

Detailed Description of the Invention

The present invention provides techniques for forming ceramic solid structures from ceramic precursors of these structures, using elastomeric molds, and structures produced according to the techniques. A variety of structures useful in microanalytical, microelectronic, micromechanical, chemical, medical and biomedical fields can be produced according to the techniques. Furthermore, the present invention provides techniques for easily reproducing intricate microscale ceramic solid structures consistently.

The ceramic solid structures of the invention, for example borosilicon carbonitride, can be used in applications where light weight, high chemical resistance, high oxidative resistance, and/or high temperature thermal stability are required properties. There are a small number of materials such as silicon carbide, silicon nitride, and metal alloys which can maintain their mechanical strengths at high temperatures, typically exceeding 1300 °C. Silicon carbide (SiC) and silicon nitride (Si₃N₄) are the most commonly explored materials for high temperature mechanical

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applications. However, silicon carbide, silicon nitride, and metal alloys suffer several drawbacks at high temperatures. Silicon carbide and silicon nitride are difficult to fabricate, undergo phase transformations, and degrade mechanically at temperatures above 1400 °C. Metal alloys, such as nickel aluminum-based materials, used for high temperature mechanical applications are also not effective at high temperatures. Metal alloys usually fail structurally or melt at temperatures above 1395 °C.

On the other hand, ceramics, such as borosilicon carbonitride, can maintain their structural integrity at temperatures exceeding 2000 °C in an inert atmosphere. In air, ceramics have excellent oxidative stability and are able to withstand temperatures greater than 1050 °C for longer than two hours. It has also been shown that ceramics can sustain their oxidative stability in air at temperatures up to 1500 °C. Even under these extreme conditions, ceramics maintain their density. For example, borosilicon carbonitride, maintains its low density of approximately 1.8 grams per cubic centimeter at high temperatures. In addition, when ceramics are exposed to harsh environments, they are able to maintain their structural integrity. One indicator of a ceramic's ability to maintain its structural integrity is its Young's modulus. The Young's modulus is a measure of strain, expressed by the ratio of a stress on a given unit of a substance to an accompanying distortion. It is a feature of the invention that the Young's modulus does not change significantly when a ceramic solid structure of the invention is exposed to harsh environments.

Another test to determine the oxidative stability of a ceramic solid structure is to expose the ceramic solid structure to an oxidative environment at high temperature. The ceramic article is then cooled down to 25 °C. Next, a scanning electron micrograph (SEM) is taken of the ceramic solid structure. The absence of structural defects appearing on the ceramic solid structure as seen on the SEM image is a good indication of the thermal and oxidative structural integrity of the ceramic solid structure.

The invention utilizes an elastomeric mold comprising an indentation pattern that can be used to transfer a ceramic precursor of a ceramic structure from the mold to a substrate surface or that can serve as a mold that when, positioned proximate to a surface of the substrate, can define a region in which the ceramic precursor is positioned. As used herein, "elastomer" describes a compound which exhibits rubbery

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properties. In other words, an elastomeric compound will recover most of its original dimensions after extension or compression.

The substrate can be any surface known in the art and can even be another mold.

5 In one embodiment, the ceramic precursor is comprised of three or more different atom types and preferably at least four different atom types such that a quarternary ceramic results. An illustrative example of atoms types which can be found in the ceramic precursor are: carbon, nitrogen, boron, silicon, phosphorus, aluminum, and/or hydrogen. The ceramic precursor can be monomeric, oligomeric or polymeric.

10 Fig. 1 illustrates schematically a technique for forming the ceramic structure at the substrate surface. An article 20, which serves generally as the elastomeric mold, includes an application surface 22 including a plurality of indentations 24 that together define a linear, patterned array of indentations contiguous with a contact surface 26. In one embodiment, after forming article 20, article 20 is treated, for example by
15 silanization with an agent that is not reactive with the ceramic precursor. This allows removal of the mold from a resulting solid without causing destruction of the solid. For example silanization prevents the ceramic structure 38 from adhering to article 20. This treatment can be accomplished with a variety of agents, such as alkylating, silylating, fluoroalkylating, or alkylsilylating agents. Article 20, according to one embodiment, is
20 a mold or an applicator used to transfer the precursor of the ceramic structure, in a linear pattern, to a region or regions proximate the substrate surface. Article 20 also can define a forming article or micromold placed proximate the substrate surface and used to guide the ceramic precursor of the ceramic structure so as to position the ceramic precursor in a pattern at a predetermined region or regions proximate the
25 substrate surface. As used herein, the term "proximate" is meant to define at the substrate surface, that is, in contact with the substrate surface, or at a position near the substrate surface and fixed relative to the substrate surface.

When article 20 is placed proximate a surface 28 of a substrate 30, contact surface 26 of the article seals portions of the surface 28 that it contacts, thereby forming
30 channels 32 defined by indentations 24 and portions 34 of the substrate surface 28 not contacted by the contact surface 26. In this manner a micromold is created, which is defined by the article 20 and the substrate surface 28. A ceramic precursor 36 of a

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ceramic structure is placed adjacent one or more openings of the channels 32 and introduced into the channels 32 and allowed to flow adjacent portions 34 of the substrate surface 28 in register with the indentations 24. The ceramic precursor 36 can be urged to flow via, for example, pressure applied to the ceramic precursor as it is positioned so as to enter the channels, or vacuum created within the channels by, for example, connection of the outlets of the channels to a source of vacuum.

Alternatively, according to one aspect of the invention, the ceramic precursor can be allowed to flow into the mold via capillary action. Capillary filling of the mold is especially useful when the mold is of very small dimension (in particular in the micro scale) and is defined herein to mean that when a ceramic precursor is positioned adjacent an opening or the channel 32 formed by a portion 34 of the substrate surface and the indentation 24 of article 20, the ceramic precursor will flow into at least a portion of the channel spontaneously. In alternate embodiments, the filling step is performed under an inert atmosphere and/or moisture-free atmosphere. As used herein, "inert" means almost entirely or entirely unreactive. In addition, as used herein "moisture free" means an environment which has less than 0.1% water or even up to less than 1% water.

Subsequent to introduction of the ceramic precursor 36 into channel 32, the ceramic precursor 36 can be solidified, or cured, before removal of article 20 from the substrate surface 28. The curing step is generally carried out to partially or fully cross-link the ceramic precursor, or polymerize a precursor that can include monomeric or oligomeric species. In one embodiment, the thermal setting or curing temperature is greater than 100 °C. In another embodiment, the ceramic precursor is cured chemically. When cured chemically, the curing step can be performed under an inert atmosphere and/or under a moisture free environment.

The article 20 can be removed by peeling article 20 off of the cured ceramic precursor 36. In an alternate embodiment, article 20 is removed from the cured ceramic precursor 36 by dissolving article 20. In a further embodiment, article 20 is dissolved using a solution containing a fluoride anion provided by compounds such as tetrabutylammonium fluoride. The cured ceramic precursor 36 can then be heated usually at a temperature greater than the thermal curing temperature. In an alternate embodiment, the cured ceramic precursor 36 can be heated without removing the

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article 20. It is during the heating step that two changes can occur to the cured ceramic precursor. First, the ceramic precursor undergoes a polymerization reaction. Second, the ceramic precursor will be pyrolyzed. As used herein, "pyrolyzation" means treatment of a ceramic precursor to reaction conditions, such as high temperature.

5 Under these reaction conditions, a material which undergoes pyrolysis may have any one or a combination of any of solvent, gases, heteroatoms, and/or functional groups removed. In addition, ceramics which undergo pyrolysis may undergo a reorganization of the atomic matrix. After heating, the article 20 is removed from the heated ceramic precursor 36.

10 The pattern of parallel indentations 24 formed in the surface 22 of the article 20 is for illustrative purposes only. Any pattern, for example a pattern defined by a single indentation or many indentations, one or more of the indentations defining a non-linear pathway of uniform or non-uniform depth, is intended to fall within the scope of the invention. Various patterns are illustrated in subsequent figures. The indentation
15 pattern can be of a variety of dimensions and, according to one aspect of the invention, includes a region having a dimension of less than 100 μm . The dimension can be a lateral dimension or vertical dimension. "Lateral dimension" is meant to define a dimension parallel to application surface 22. "Vertical dimension" is meant to define a dimension perpendicular to the surface. A lateral or vertical dimension can be a
20 dimension of a feature that is a portion of an overall structure. That is, an overall structure could have a width of 5 millimeters parallel to the surface and a height of 5 millimeters relative to the surface, but include a ridge on the top of the structure of 75 μm height and 75 μm width. That sub-feature would, by definition, have a lateral dimension of 75 μm and a vertical dimension of 75 μm . According to preferred
25 embodiments, the indentation pattern includes a portion having a dimension of less than about 100 μm , less than about 50 μm , less than about 30 μm , less than about 20, 15, 10, 5 or 1 μm . The dimension of the indentations can be altered by deforming the article 20.

Where the article 20 is placed adjacent to the substrate surface 28 and the
30 ceramic precursor fills channels 32, ceramic structure or structures 38 resulting from the technique can have lateral dimensional features that correspond to the lateral dimensional features of indentations 32 of the article. For some structures, it is not

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necessary that the ceramic precursor completely fill the channels 32 and some minute flaws may be tolerated. In other embodiments in which channels 32 may not be completely filled, the lateral dimension of ceramic article 38 formed from the ceramic precursor is to be minimized. According to this embodiment, ceramic precursor 36 is introduced into the channels 32 in an amount small enough that the ceramic precursor wets only the corners of the channels. When the ceramic precursor, substrate, and article are selected such that the ceramic precursor will wet the micromold efficiently via capillary action, when a small amount of ceramic precursor is supplied to the article channel or channels, the ceramic precursor will selectively wet portions of the channels having a low interior angle relative to the rest of the channel (such as corners 39 defined by the abutment of contact surface 26 against the substrate surface 28 at the edge of region 34 of the substrate surface). When the ceramic precursor wets the corners selectively and the ceramic precursor is heated to form the ceramic structure, the resulting structure can define a pattern having a dimension smaller than that of the lateral dimension of indentation 24. According to this embodiment the lateral dimension of structure 38, at its narrowest, is narrower than the narrowest lateral dimension of channel 24 of the article, and can have a height significantly less than the height of the channel. The lateral dimension of the ceramic structure 38 according to this embodiment can be on the order of less than or equal to about 100 μm or 50 μm , or preferably less than about 20 or 10 μm , more preferably less than about 5 μm or 1 μm .

Any suitable material can define the substrate 30 of the invention. The substrate surface 28 can be of the same material as the bulk material of substrate 30, or a different material. Substrates exposing a variety of functional surfaces such as hydrophobic, hydrophilic, and biologically compatible or non-compatible surfaces are known, and are suitable for use with the invention. In other embodiments, free-standing ceramic structures are formed. In particular, a silicon wafer carrying a fluorosilane film is particularly useful. Other substrate materials include silicon, silicon dioxide, silicon nitride, polymers and metals such as gold and chromium. In a further embodiment, the substrate is treated so that it is inert. Article 20 similarly can be formed of a variety of materials. According to one embodiment, substrate surface 28 and/or contact surface 26 of article 20 is an elastomer or other conformable material. Preferably, contact surface 26 and more preferably, for ease of fabrication, the entire

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article 20, is formed of an elastomer, most preferably polydimethyl siloxane (PDMS). When the elastomer defines substrate surface 28 or contact surface 26, or preferably article 20, an optimal seal is created between contact surface 26 and portions of the substrate surface 28 adjacent and contiguous with portions 34 that with the indentations 5 24 define the channels 32. This results in optimal confinement of the ceramic precursor 36 to the channels 32. According to the invention pressure can be applied to the article 20 against the substrate 30 during micromolding, but according to embodiments in which an elastomer is used as described, pressure need not be applied as the elastomer conforms well to the surface against which it mates thus sealing the channels 32. The 10 article 20 can be fabricated of an elastomer in a manner analogous to the fabrication of a stamp from an elastomer as described in co-pending, commonly-owned U.S. Application Serial No. 08/131,841 by Kumar, et al, entitled "*Formation of Microstamped Patterns on Surfaces and Derivative Articles*", filed 4 October 1993, and incorporated herein by reference.

15 Fig. 2 illustrates another embodiment of the invention in which, rather than forming ceramic structures via micromolding, a microtransfer molding technique is used to transfer a set of patterns, in parallel, to a substrate surface 28 (parallel molding of a variety of similar patterns via micromolding as illustrated in Fig. 1 is embraced by the invention as well). In Fig. 2 a transfer article 40, which can be made of the same 20 material from which article 20 is made, includes a plurality of indentation patterns 42 that can be identical. Application of the ceramic precursor 36 to the plurality of indentation patterns 42, followed by positioning the indentation patterns of the applicator adjacent the substrate surface 28, results in transfer of the ceramic precursor, in the pattern, to the substrate surface 28. Heating can take place prior to or after 25 removal of the article 40 from the substrate surface 28, preferably after removal of the article following brief, mild heating. Specifically, ceramic precursor 36 is applied to the indentation patterns 42 preferably by coating the surface 41 with ceramic precursor 36, spreading the ceramic precursor back and forth across the surface 41 with an applicator to assure filling of each of the indentations 42, and removal of excess 30 ceramic precursor until a small drop of the ceramic precursor is left essentially in the center of the indentation pattern. Then, the surface 41 of the applicator is brought into contact with the substrate surface 28 to transfer the ceramic precursor, in the pattern, to

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the substrate surface 28. At this point, the substrate and applicator are, together, gently thermally cured to, for example, 150° C by gradually raising the temperature for one hour, and then the applicator 40 removed, leaving a plurality of pre-heated ceramic precursors 44, arranged in patterns corresponding to the indentation patterns 42 of applicator 40, on the substrate surface 28. Following heating under an inert atmosphere, ceramic microstructures 46 can be allowed to remain on the substrate surface 28, or can be removed from the substrate surface 28 to define free-standing articles.

According to the embodiment illustrated in Fig. 2, the ceramic precursor 36 of the ceramic articles 46 is transferred essentially instantaneously to the substrate surface 28, in the indentation pattern 42.

As used herein, "ceramic solid structure" includes a class of materials comprising inorganic, nonmetallic solids which can withstand high temperatures during manufacture and use. An example of a ceramic solid structure would be borosilicon carbonitride (SiBNC).

Borosilicon carbonitride (SiBNC) can be synthesized from several preceramic polymers. Borosilicon carbonitride ceramics have several beneficial characteristics which make them useful for applications under high temperature conditions. Borosilicon carbonitride materials are light weight and stable at temperatures exceeding 2000 °C in an inert atmosphere. They also show excellent resistance to oxidation at temperatures up to 1500 °C in air.

In one embodiment, the ceramic article demonstrates structural integrity when exposed to harsh oxidative and thermal conditions. In another embodiment of the invention, the ceramic article is structurally stable when exposed to harsh oxidative and thermal conditions as demonstrated by an SEM analysis of the ceramic article. In a further embodiment, the ceramic article demonstrates its structural integrity upon being exposed to air for two hours at 1050 °C as demonstrated by SEM analysis of the ceramic article.

In a preferred embodiment, the ceramic article's Young's modulus will not change more than 10% upon heating to 1400 °C in an inert atmosphere. In another preferred embodiment, the ceramic article's Young's modulus will not change more than 10% upon heating to 1400 °C in air. In a further preferred embodiment, the

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Young's modulus at 25 °C will not change by more than 10% upon heating the ceramic article to 1400 °C followed by cooling the ceramic article down to 25 °C.

A simple screening test for determining useful precursors of ceramic materials of the invention involves providing a known precursor and testing its viscosity to
5 determine whether it can fill a mold having dimensions on the order of dimensions desired in a final ceramic structure. If the material is too viscous, it can be determined whether viscosity can be lowered by dilution with a suitable solvent, preferably a low-boiling solvent that can be driven off via gentle heating prior to pyrolyzation and condensation. In another embodiment, viscosity of the ceramic precursor is controlled
10 by a reaction with ammonia. In an alternate embodiment, a ceramic precursor viscosity of less than 500 cm²/s is sufficient.

Fig. 3 is a photocopy of two SEM images of the same free-standing, ceramic solid structure 46, fabricated in accordance with the technique of Fig. 1. By use of the term "free-standing", it is meant that the structure need not be supported by a substrate,
15 and is not an integral part of a substrate. The structure has a variety of different feature sizes. Structure 46 is a hexagonal grid with a vertical dimension of approximately 50 µm and a lateral dimension of approximately 20 µm.

Fig. 4 is a photocopy of three SEM images of the same free-standing, ceramic solid structure 66. However, the ceramic structure of Fig. 4 has been heated in air to
20 1050 °C for two hours. Fig. 4 demonstrates the high oxidative stability of ceramics at high temperatures as no obvious oxidative defects are seen in the SEM images.

Fig. 5 is a photocopy of two SEM image of another free-standing, ceramic solid structure 66. Structure 66 is a hexagonal grid with a lateral dimension of approximately 70 µm.

25 Fig. 6 is a photocopy of three SEM image of the same free-standing, ceramic solid structure 76. Structure 76 is a micron scale tooth of a gear with an aspect ratio of approximately 3-4 to 1.

The technique of the invention can be carried out on nonplanar, for example, curved surfaces when a flexible or elastomeric applicator (20/40) is used. Where a
30 nonplanar substrate 28 exists, a flexible or elastomeric applicator 20 or 40 can be bent to conform to the nonplanar substrate surface 28 and the technique carried out as described. Where the ceramic precursor 36 of a ceramic solid structure is viscous

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enough, the nonplanar substrate, such a cylindrical article (capillary or the like) can be rolled across the surface 41 or 22 of applicator 40 or 20, respectively, the pattern transferred to the nonplanar article, and the ceramic structure heated on the surface of the article.

5 Example ceramics that can be made in accordance with the invention include SiCN, SiC, SiN, BN and SiAlCN.

 The function and advantage of these and other embodiments of the present invention will be more fully understood from the examples below. The following examples are intended to illustrate the benefits of the present invention, but do not
10 exemplify the full scope of the invention.

Example 1: Fabrication of Ceramic Structure Molds

 The photomasks used for the fabrication of masters were transparency films having opaque patterns of features printed by a high-resolution printer (≥ 3386 dpi). The
15 masters were fabricated using SU-8 photoresist (MicroChem Corp., Newton, MA) on silicon wafers (Test grade, Silicon Sense, Inc., Nashua, NH) by conventional photolithographic techniques. The bas-relief masters of SU-8 were silanized in a dessicator that was connected to a vacuum, and contained a vial with small amount of (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane. The silanization was used to
20 prevent adhesion of PDMS to the masters. Casting prepolymer, Sylgard 184 (Dow Corning, Midland) on these silanized masters and curing at 70 °C formed the PDMS molds with bas-relief structures as negative replicas of the structures in the SU-8. The PDMS molds were heated at 160 °C in an oven for ~2 h to complete the cure. The surface of the PDMS mold was oxidized with an oxygen or air plasma in a plasma
25 cleaner (SPI Plasma PREP II™; www.2spi.com) at a pressure of ~1 mm Hg for 2 min. These molds were then exposed to vapors of (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane for ~12 h to obtain hydrophobic surfaces. Polished silicon wafers were used as substrates and treated with oxygen plasma and silanized by the aforementioned reagent prior to use.

30

Example 2: Synthesis of Polymeric Ceramic precursor

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All syntheses were performed under an argon atmosphere in Schlenk-type glassware. The polymeric precursor was synthesized from 1-(trichlorosilyl)-1-(dichloroboryl)ethane (TSDE). The duration of the polymerization was adjusted under an ammonia atmosphere in order to obtain a preceramic polymer with a suitable viscosity for microtransfer molding (μ TM) and vacuum assisted micromolding in capillaries (MIMIC) at temperatures of 120-140 °C. The product was a colorless transparent glass-like solid at room temperature. At 120 °C, the preceramic polymer has a viscosity similar to that of thick honey.

10 Example 3: Synthesis of 1-(Trichlorosilyl)-1-(dichloroboryl)ethane (TSDE)

Boron trichloride (99.9%, Aldrich, 0.1 mol, ~9 mL at -78 °C) was condensed at -65 °C in a round-bottom flask equipped with an addition funnel. Trichlorovinylsilane (97%, Aldrich, 0.1 mol, ~13 mL) was pre-mixed with triethylsilane (99%, Aldrich, 0.1 mol, ~16 mL), and added dropwise to BCl_3 over 15 min. The mixture was stirred for one hour and then allowed to warm to room temperature. The reaction mixture was distilled using a Vigreux column at ~40 °C/12 mbar to obtain TSDE. The product is a colorless liquid at room temperature and extremely sensitive to moisture and air. (*Caution: BCl_3 is highly corrosive and should be handled with care.*)

20 Example 4: Synthesis of the Preceramic Polymer

TSDE (~0.06 mol) was added dropwise to a solution of ~60 mL of methylamine (anhydrous, 98+%, Aldrich) in ~180 mL of dry hexane (100.0%, A.C.S. reagent, J. T. Baker, Phillipsburg, NJ) at -65 °C under argon. The mixture was allowed to react overnight under vigorous stirring. After reaction was complete, the mixture was warmed to room temperature, and a white solid was removed by filtration using house vacuum. Hexane was removed by distillation from the filtrate using a rotary evaporator (Model: R110, Büchi) under moderate vacuum (~20 mm Hg). This polymer was heated for 1-2 h at 100 °C under an atmosphere of ammonia, followed by degassing under vacuum (~3 mm Hg) for 30 min. Upon cooling to room temperature, a colorless glassy solid was obtained and stored under argon.

Example 5: Fabrication of Microstructures of SiBNC Ceramics

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The manipulations were conducted in a glove bag under argon. The fabrication of preceramic microstructures using μ TM involves the following steps: (i) Silanized PDMS molds were placed on a hot plate with their structured surface facing upward. The temperature of the hotplate was set at 120 °C; (ii) A flask containing preceramic polymer 1 was heated on the hotplate. After this polymer melted into a viscous liquid, it was transferred onto the top of the molds using a spatula; (iii) After the polymer filled the voids of the PDMS mold, a silanized silicon wafer was placed on the top. A pressure of ~5 psi ($\sim 3 \times 10^4$ Pascals) was applied on the wafer using a weight; (iv) The temperature of the hotplate was then raised to 200 °C at a rate of 2 °C/min. The polymer was cured at this temperature for 1 h and cooled to room temperature on the hotplate. An alternative process used vacuum assisted MIMIC. In this method, a PDMS mold was placed directly against the surface of a silanized silicon substrate on a hotplate. The preceramic polymer was melted at 120 °C and transferred to the entrance of the PDMS mold using a spatula. The channels were filled with the polymer by applying vacuum in the channels and by capillary flow. The hotplate was heated to 200 °C, held at that temperature for 1 h, and cooled to room temperature.

Once the hotplate was cooled down, we first tried to peel off the PDMS mold from the silanized substrate and from the preceramic microstructure. The mold could sometimes be removed from the substrate, leaving the preceramic microstructures still attached to the silicon substrate. In these cases, the preceramic structures along with the substrate were transferred into a quartz tube furnace for pyrolysis and condensation. When the PDMS molds could not be peeled off from the polymeric microstructures, we used a 1.0 M TBAF solution in THF (Aldrich) to dissolve the PDMS mold. In this case, the microstructure and the PDMS mold were normally released from the silanized substrate first. The preceramic microstructure became freestanding after the dissolution of the PDMS mold by the TBAF solution. This freestanding preceramic structure was placed on top of a silicon substrate and transferred into the quartz tube furnace for pyrolysis and condensation.

The conversion of polymeric microstructures into ceramics started with the purge of the samples positioned in the center of a quartz tube with argon for ~ 15 min. The temperature of the furnace (model: TF55035A, Linderberg/Blue) was raised to 1050 °C at a rate of 1 °C/min and held for 2 h at that temperature. After the heating,

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the furnace was cooled to room temperature at a rate of 2 °C/min. If the preceramic structures were freestanding, the final ceramic structures could be easily removed from the silicon substrate. Some microstructures that were initially attached to the silanized silicon substrate released spontaneously. The test of thermal stability of the ceramic

5 microstructure was performed using a freestanding microstructure of hexagonal honeycomb grid following a similar heating procedure but in air.

Those skilled in the art would readily appreciate that all parameters listed herein are meant to be exemplary and that actual parameters will depend upon the specific application for which the methods and apparatus of the present invention are used. It

10 is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described.

What is claimed is:

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CLAIMS

1. A method comprising:
providing a mold having at least one component with at least one dimension
5 less than 100 μm ; and
filling the mold with a ceramic precursor.
2. The method of claim 1, wherein the ceramic precursor comprises at least two
different atom types.
10
3. The method of claim 2, wherein the at least two different atom types are
selected from a group consisting of carbon, nitrogen, boron, silicon, phosphorus,
aluminum and hydrogen.
- 15 4. The method of claim 1, wherein the ceramic precursor comprises at least three
different atom types.
5. The method of claim 1, further comprising heating the ceramic precursor to
produce a ceramic structure.
20
6. The method of claim 5, wherein each atom type of the ceramic structure is
derived from the ceramic precursor.
7. The method of claim 5, wherein the step of heating is performed under an inert
25 atmosphere.
8. The method of claim 5, wherein the step of heating is performed under a
moisture-free atmosphere.
- 30 9. The method of claim 1, wherein prior to the step of filling, the ceramic
precursor is prepared to have sufficient viscosity to completely fill the mold.

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10. The method of claim 9, wherein the viscosity of the ceramic precursor is adjusted to have a value less than about 500 cm²/s.
11. The method of claim 1, wherein prior to the step of filling, the mold is treated
5 such that it is inert with respect to reaction with the ceramic precursor and any subsequent products resulting from the ceramic precursor.
12. The method of claim 11, wherein the step of treating the mold comprises reacting the mold with an agent selected from the group consisting of alkylating,
10 silylating, fluoroalkylating, or alkylsilylating agent.
13. The method of claim 1, wherein the step of filling comprises positioning a surface of the mold against a surface of a substrate to create a cavity which the ceramic precursor fills.
15
14. The method of claim 13, wherein the substrate is selected from the group consisting of silicon, silicon dioxide, silicon nitride, and any substrate with a smooth metallic surface.
15. The method of claim 13, further comprising treating the substrate surface to
20 render the substrate inert with respect to reaction with the ceramic precursor and any subsequent products resulting from the ceramic precursor
16. The method of claim 15, wherein the step of treating comprises silanization.
25
17. The method of claim 1, wherein the step of filling comprises allowing the ceramic precursor to enter a volume of lower pressure.
18. The method of claim 1, wherein the step of filling comprises allowing the
30 ceramic precursor to enter a volume by means of capillary action.
19. The method of claim 1, further comprising the step of curing the ceramic

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precursor in the mold.

20. The method of claim 19, wherein the ceramic precursor is cured chemically.

5 21. The method of claim 19, wherein the ceramic precursor is cured thermally.

22. The method of claim 19, wherein the ceramic precursor is cured in the mold at a temperature of at least 100 °C.

10 23. The method of claim 19, wherein the ceramic precursor is cured in the mold under an inert atmosphere.

24. The method of claim 19, wherein the precursor is cured in the mold under a moisture-free atmosphere.

15

25. The method of claim 1, further comprising removing the mold from a product formed from the ceramic precursor.

20 26. The method of claim 25, wherein the step of removing the mold comprises physically removing the mold.

27. The method of claim 25, wherein the step of removing the mold comprises dissolving the mold.

25 28. The method of claim 27, wherein the step of dissolving comprises dissolving the mold in a solution containing fluoride anions.

29. The method of claim 28, wherein the solution contains tetrabutylammonium fluoride.

30

30. The method of claim 25, wherein the product comprises a cured ceramic precursor and after removing the mold, the method further comprises heating the cured

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ceramic precursor to a temperature of at least 1000 °C to produce a ceramic.

31. The method of claim 25, further comprising transferring the product to a substrate selected from the group consisting of silicon, silicon dioxide, silicon nitride, and metal.
32. The method of claim 1, wherein the ceramic precursor is a single precursor.
33. The method of claim 1, wherein the ceramic precursor comprises a polymer.
34. The method of claim 1, wherein the ceramic precursor comprises an oligomer.
35. The method of claim 1, wherein the mold exhibits elastomeric properties.
36. The method of claim 35, wherein the mold comprises polydialkylsiloxane material.
37. The method of claim 1, wherein the step of filling the mold is performed under an inert atmosphere.
38. The method of claim 1, wherein the step of filling the mold is performed under a moisture-free atmosphere.
39. An article comprising a free standing ceramic structure with at least one component with a dimension less than 50 μm , the at least one component being integral with the article.
40. The article of claim 39, wherein the article is a molded article.
41. The article of claim 39, wherein the ceramic comprises a formula $\text{Si}_w\text{B}_x\text{N}_y\text{C}_z$.
42. The article of claim 39, wherein the ceramic has an oxide content of less than

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about 30% by atomic composition.

43. The article of claim 39, wherein the ceramic is substantially free of structural degradation upon exposure to air at a temperature of greater than 1000 °C for at least 2
5 hours.

44. The article of claim 39, wherein the at least one component has an aspect ratio of at least about 2:1.

10 45. The article of claim 39, wherein the at least one component has an aspect ratio of at least about 4:1.

46. The article of claim 39, wherein the article is capable of withstanding temperatures greater than 2000 °C.

15

47. The article of claim 39, wherein the article can withstand temperatures less than 1500 °C in the presence of air for at least about 80 hours resulting in a change of less than a 10% in Young's Modulus of the article.

20 48. The article of claim 39, wherein the at least one component has a dimension less than 25 µm, the at least one component being integral with the article.

49. The article of claim 39, wherein the at least one component has a dimension less than 15 µm, the at least one component being integral with the article.

25

50. A method comprising:
providing a mold;
silanizing the mold; and
filling the mold with a ceramic precursor.

30

51. A method comprising:
providing a mold;

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filling the mold with a ceramic precursor; and
dissolving the mold.

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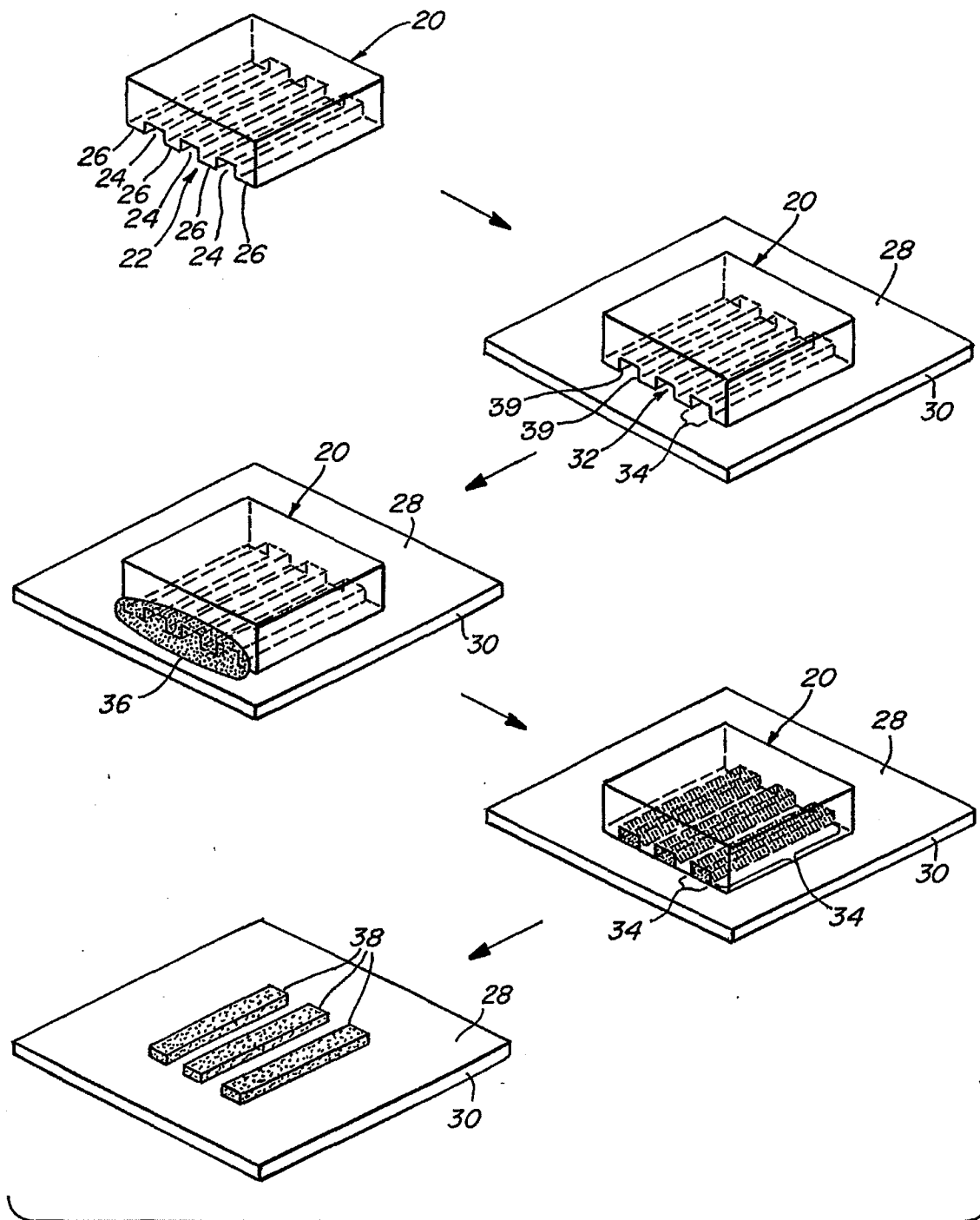


Fig. 1A

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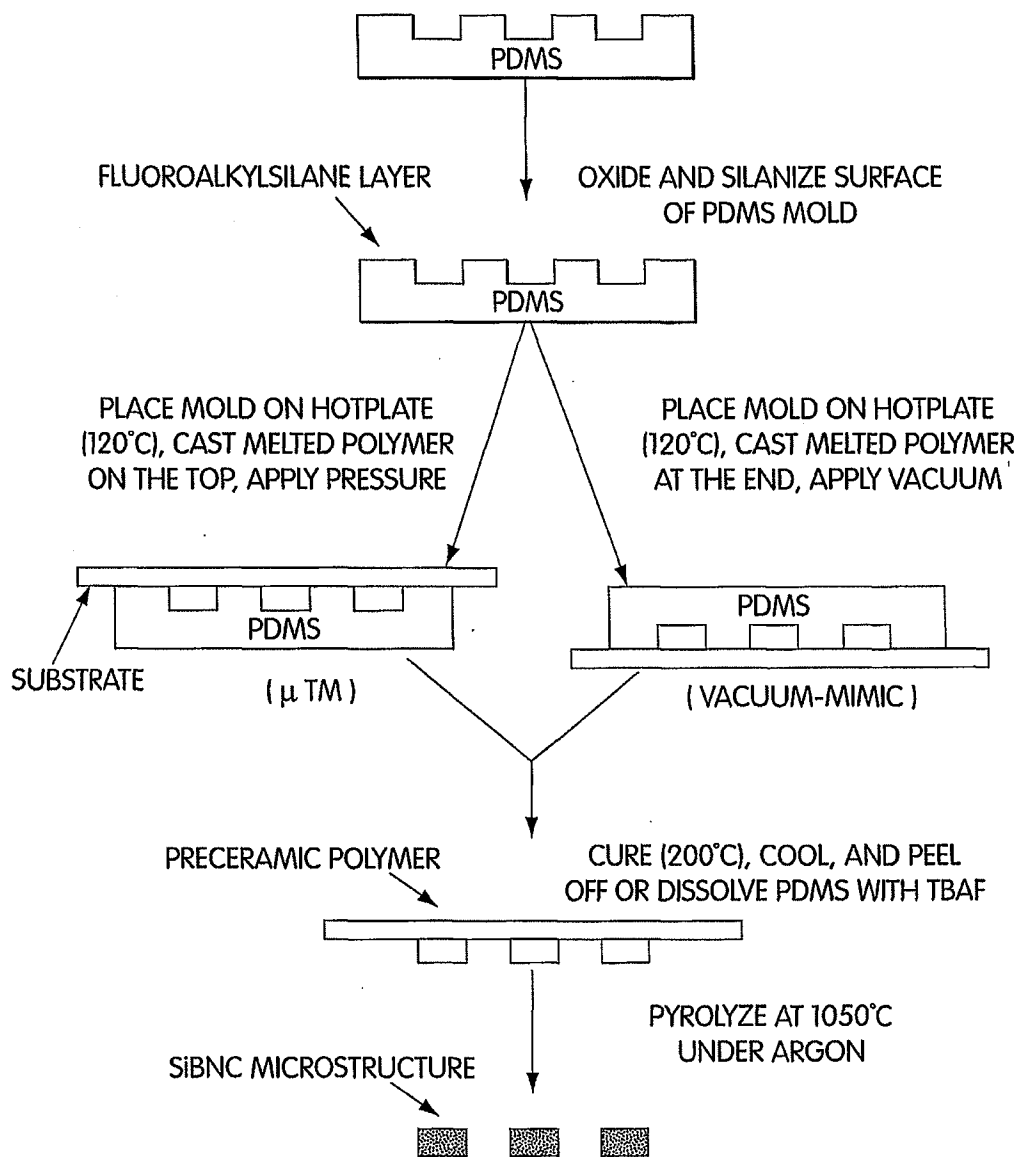


Fig. 1B

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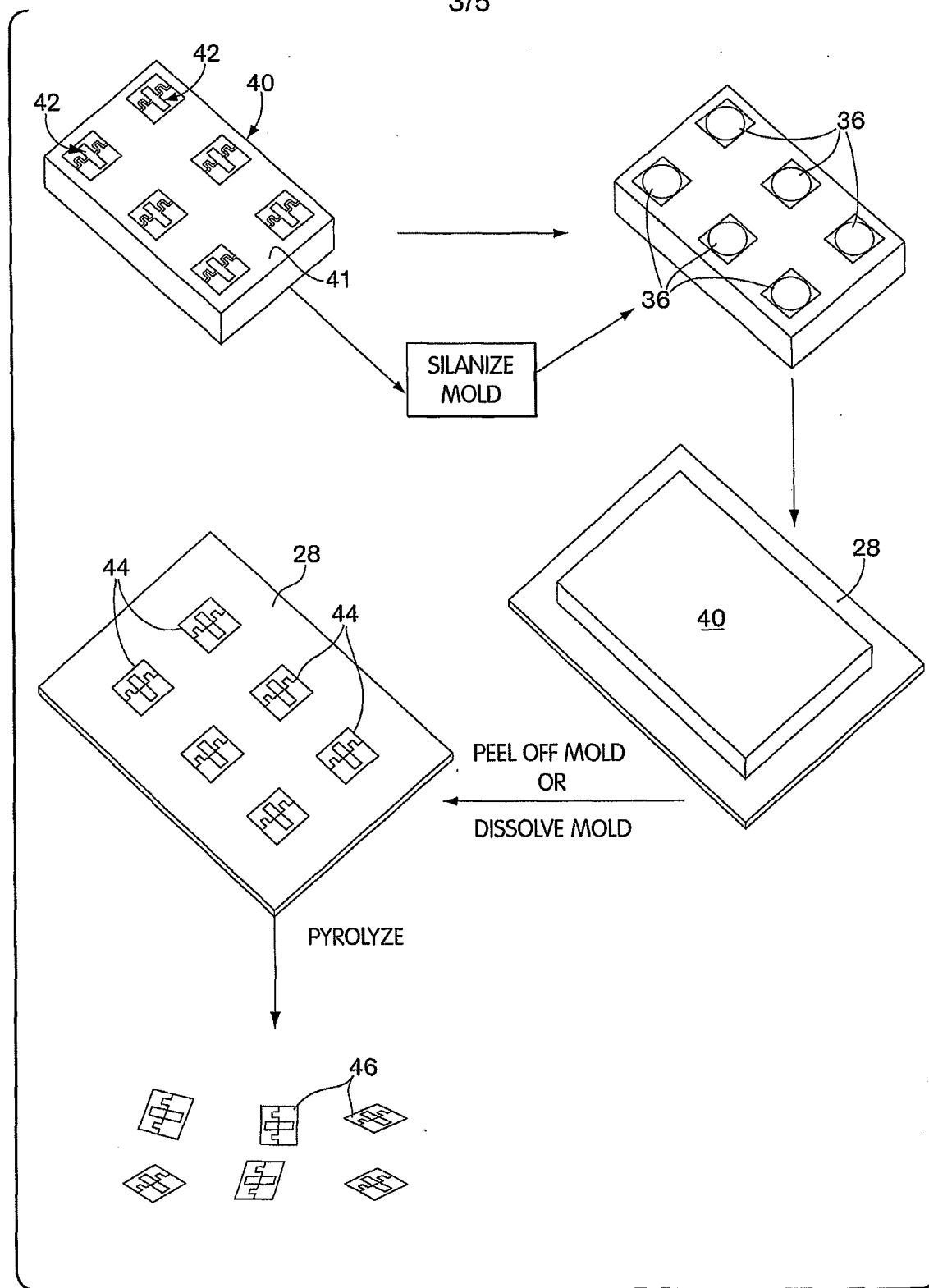
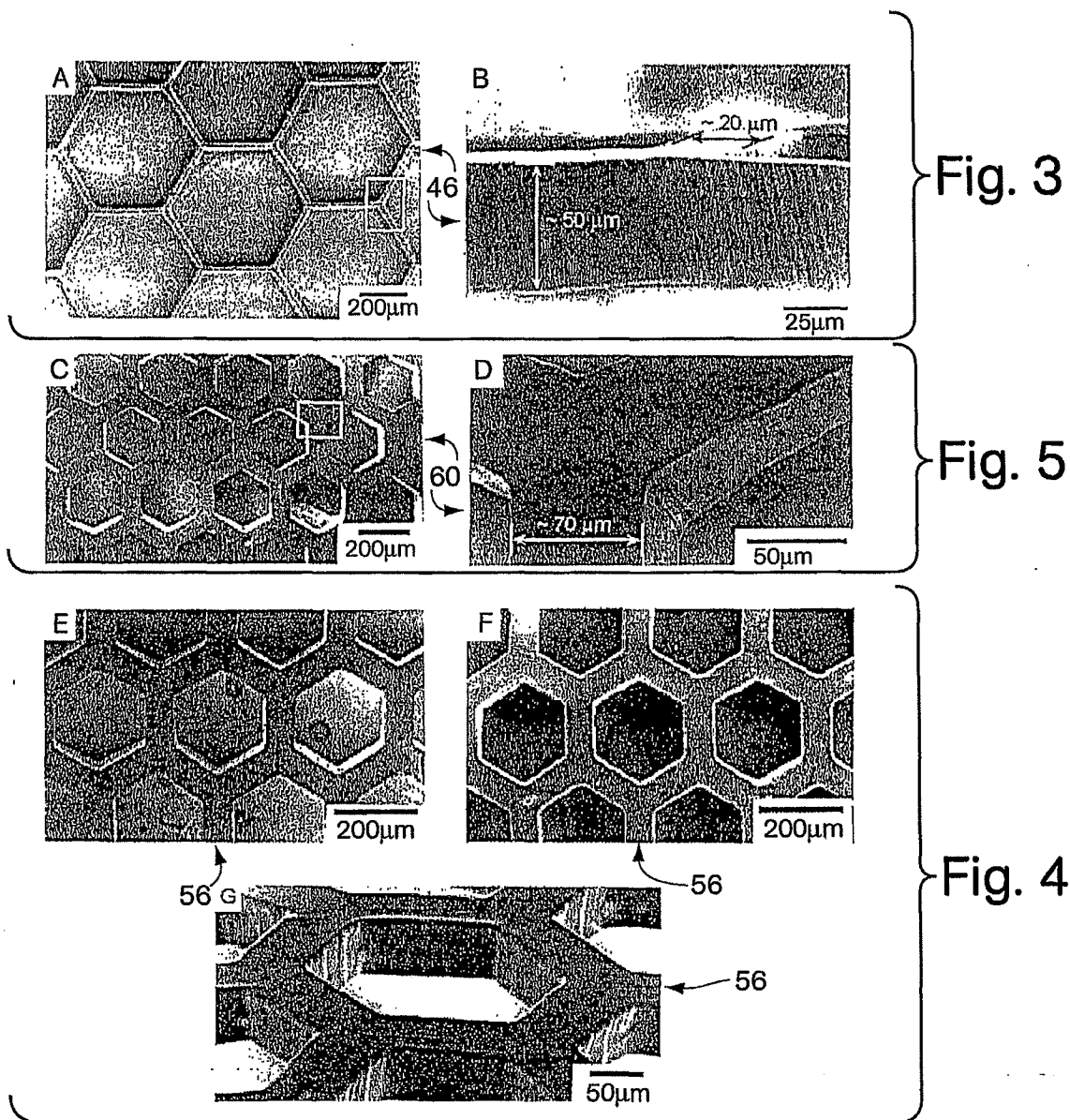


Fig. 2

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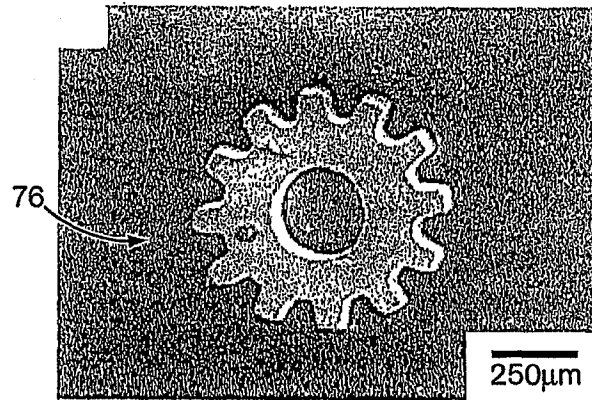


Fig. 6a

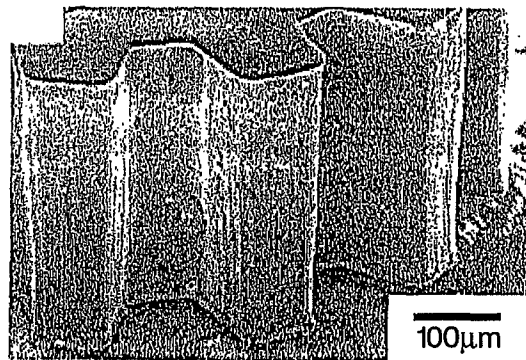


Fig. 6b

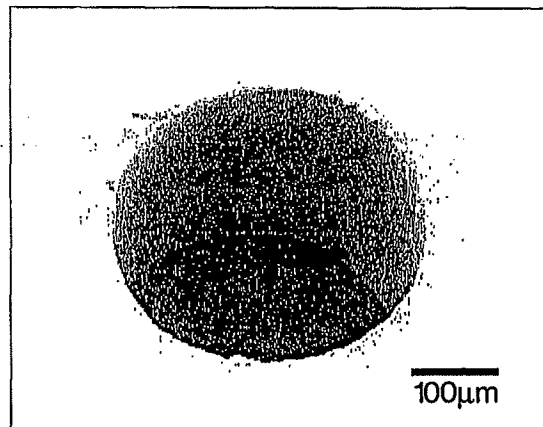


Fig. 6c

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/26830

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C04B35/622 C04B35/571 C04B35/589 B28B11/24 B28B13/02
B28B7/34 B28B7/38 G03F7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C04B B28B G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 196 05 521 C (KARLSRUHE FORSCHZENT) 3 July 1997 (1997-07-03)	1-10, 17, 19, 25-27, 30, 32-34, 39, 40, 43, 46, 48, 49, 51
Y	column 2, line 46-55; examples 1, 3	
Y	example 1	11, 12
	example 1	16, 50

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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

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E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

22 January 2002

Date of mailing of the international search report

05/02/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

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INTERNATIONAL SEARCH REPORT

Inter ☐ nal Application No

PCT/US 01/26830

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>FREIMUTH H ET AL: "FORMATION OF COMPLEX CERAMIC MINIATURIZED STRUCTURES BY PYROLYSIS OF POLY(VINYLSILAZANE)" JOURNAL OF THE AMERICAN CERAMIC SOCIETY, AMERICAN CERAMIC SOCIETY, COLUMBUS, US, vol. 79, no. 6, 1 June 1996 (1996-06-01), pages 1457-1465, XP000596068 ISSN: 0002-7820 abstract page 1459, left-hand column, paragraph 2 - paragraph 5 page 1464, left-hand column, paragraph 1 -right-hand column, paragraph 1; figures 10-12</p>	<p>1-9, 17, 25, 30, 32, 33, 37-40, 42-46, 48, 49</p>
X	<p>HRUBY J M ET AL: "LIGA: METALS, PLASTICS, AND CERAMICS" PROCEEDINGS OF THE SPIE, SPIE, BELLINGHAM, VA, US, vol. 3874, September 1999 (1999-09), pages 32-43, XP000951438</p> <p>page 38, paragraph 3.2 page 41, paragraph 4.2</p>	<p>1, 2, 4-6, 9, 17, 19, 21, 22, 25-27, 30, 32, 33, 39, 40, 43-46, 51</p>
X	<p>WO 00 26157 A (UNIV CALIFORNIA) 11 May 2000 (2000-05-11)</p> <p>page 4, line 3-17; figure 2 page 6, line 16 -page 7, line 10 page 9, line 6-16; examples 1, 5, 7, 10-21</p>	<p>1-6, 9, 13-15, 17, 18, 25, 31-36, 39, 40, 44-46, 49</p>
X	<p>DE 197 12 442 A (KARLSRUHE FORSCHZENT) 1 October 1998 (1998-10-01)</p> <p>column 2, line 12-31 column 2, line 58 -column 3, line 56; example 1</p>	<p>1-10, 17, 19, 21, 25, 26, 30, 32, 33, 39, 40, 42-46, 48</p>

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/26830

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	NOEKER F ET AL: "HERSTELLUNG VON MIKROSTRUKTURKÖRPERN AUS KERAMIK" KERAMISCHE ZEITSCHRIFT, FREIBURG, DE, vol. 44, no. 10, 1992, pages 677-678, 680-681, XP000443986 the whole document	1,2,4-6, 9,10,17, 25,32, 33,35, 37,39, 40, 43-46, 48,49
X	US 5 676 906 A (HIRATA YOSHIHIRO) 14 October 1997 (1997-10-14) column 3, line 1 -column 5, line 47	1,2,4-9, 17, 25-27, 32,39, 40,42, 44,45, 48,49,51
X	US 5 735 985 A (GHOSH SYAMAL K ET AL) 7 April 1998 (1998-04-07) column 1, line 55 -column 2, line 40 column 5, line 37 -column 7, line 9	1-9,17, 25,30, 32,33, 35,39, 40, 43-46, 48,49
X	RITHHAUPT-KLEISSL ET AL.: "Development of ceramic microstructures" MICROSYSTEM TECHNOLOGIES, vol. 2, 1996, pages 130-134, XP001058362 the whole document	1,2,4-6, 9,17,19, 21, 25-27, 30-35, 37-40,51
X	US 6 039 897 A (YAGER PAUL ET AL) 21 March 2000 (2000-03-21) column 5, line 21 -column 7, line 2; examples 1,2	1,2,4,9, 13,14, 17-21, 23,25, 31,32, 35-37
X	US 5 700 411 A (GHOSH SYAMAL K ET AL) 23 December 1997 (1997-12-23) the whole document	1-9,17, 25,32
Y	GB 2 262 465 A (SECR DEFENCE) 23 June 1993 (1993-06-23) page 3, line 1-25; claim 1	11,12

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INTERNATIONAL SEARCH REPORT

Inter national Application No
PCT/US 01/26830

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>DATABASE WPI Section Ch, Week 199418 Derwent Publications Ltd., London, GB; Class A96, AN 1994-146978 XP002188002 & JP 06 090738 A (SUMITOMO BAKELITE CO), 5 April 1994 (1994-04-05) abstract</p> <p>-----</p>	16,50

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Present claims 50 and 51 relate to an extremely large number of possible methods. Support within the meaning of Article 6 PCT and disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the methods claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the methods as described in claims 50 and 51 being claims depending on claim 1.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/26830

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 19605521	C	03-07-1997	DE 19605521 C1	03-07-1997
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